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(54) [Title of invention] Cyclic Polyester Oligomer Production Method and Polyester  
Production Method

(57) [Abstract]

[Issues]

A production method of cyclic polyester oligomers in which, in a production method of polyester with a high degree of polymerization, an economic efficiency is enhanced compared to that of prior art production methods.

[Means of Resolution]

A production method of cyclic polyester oligomers, wherein, in producing cyclic polyester oligomers from straight polyester oligomers that are obtained through an esterification reaction of dicarboxylic acid components and diol components, or from straight polyester, when at least a portion of a reaction solvent which is discharged from a reaction tank in which the cyclic polyester oligomers are produced is put back to said reaction tank for repeated use, the amount of unreacted materials contained in the reaction solvent is 10% or less by weight.

[What is claimed is:]

[Claim 1]

A production method of cyclic polyester oligomers, wherein in producing cyclic polyester oligomers from straight polyester oligomers that are obtained through an esterification reaction of dicarboxylic acid components and diol components, or from straight polyester, when at least a portion of a reaction solvent which is discharged from a reaction tank in which the cyclic polyester oligomers are produced is put back to said reaction tank for repeated use, the amount of unreacted materials contained in the reaction solvent is 10% or less by weight.

[Claim 2]

The production method of cyclic polyester oligomers according to claim 1, wherein straight polyester oligomers that are obtained through an esterification reaction of dicarboxylic acid components and diol components with a starting mole ratio (the diol components/ the dicarboxylic acid components) of 1.0 ~ 1.6 is employed.

[Claim 3]

The production method of cyclic polyester oligomers according to claim 1 or claim 2, wherein an esterification reaction of dicarboxylic acid components and diol components is conducted through a continuous polymerization process.

[Claim 4]

The production method of cyclic polyester oligomers according to claim 1, wherein straight polyester is used.

[Claim 5]

The production method of cyclic polyester oligomers according to any one of claim 1 through claim 4, wherein the reaction solvent is a compound having a carbon number of 6 or more.

[Claim 6]

The production method of cyclic polyester oligomers according to any one of claim 1 through claim 5, wherein an average polymerization degree of cyclic polyester oligomers is 2 ~ 10.

[Claim 7]

A method to produce polyester in which cyclic polyester oligomers according to any one of claim 1 through claim 6 are brought into contact with a catalyst for cyclic polyester oligomers and an open ring polymerization is conducted.

[Claim 8]

The polyester production method according to claim 7, wherein the polyester is polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate or a copolymer thereof.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of Invention]

The present invention is related to an economical production method of cyclic polyester oligomers using straight polyester oligomers or straight polyester, a catalyst and a reaction solvent.

[0002]

[Prior Art Technologies]

Because of its excellent properties, polyester is used for a wide variety of areas such as for fibers, films and bottles. In particular, polyalkylene terephthalate is superior in its mechanical strength, chemical properties, dimensional stability and so forth, and thus it is preferably used. Besides, among its uses, for example, for fibers to be used in industrial materials, a high degree of strength is required. Therefore, methods to improve the fiber strength through making the molecular weight of polyalkylene terephthalate higher is suggested.

[0003]

Generally, polyalkylene terephthalate is produced from terephthalic acid or its ester formation derivative and alkylene glycol, but in a commercial process to manufacture polymers with a high molecular weight, a method in which a melt polymerization is conducted and then a solid phase polymerization is conducted to obtain a high degree of polymerization is widely applied. However, a

method to obtain a high degree of polymerization through a solid phase polymerization has some undesirable characteristics such as those which are described below.

[0004]

For instance, in order to conduct a solid phase polymerization, there is a large increase in the cost for facilities such as a process for drying polyester chips. Moreover, a residence time for chips is long. Therefore, large improvements in its productivity are desired.

[0005]

For these issues, for instance in publication No. WO96/ 22319, a method is proposed in which polyethylene terephthalate prepolymer in a molten state having a polymerization degree of 5 ~ 35 is cooled at 120 ~ 210 degrees Celsius, then pelletized and crystallized at the same time, or in which non-quality polyethylene terephthalate prepolymer in a pellet form having a polymerization degree of 5 ~ 35 is rapidly heated to 120 ~ 210 degrees Celsius and then crystallized, and a solid phase polymerization is conducted at 230 ~ 240 degrees Celsius to give polyethylene terephthalate prepolymer. With these methods, a melt polycondensation process is eliminated and a solid phase polymerization is conducted. Thereby it proposes a reduction of facility costs. However, in order to obtain a higher polymerization degree with polyethylene terephthalate prepolymer, a substantial reaction time is required in a solid phase polymerization process. Therefore, these methods are insufficient in order to improve the productivity of prior art methods.

[0006]

On the other hand, open ring polymerization reactions using cyclic polyester oligomers are attracting attentions. For example, regarding the open ring polymerization of cyclic polyester oligomers described in Macromolecules (Brunelle, 31 (4782), 1998), it is reported that polymer having a high degree of polymerization can be obtained in a very short period of time. In the report, diol and terephthaloyl chloride are employed as source materials and condensation is conducted under a presence of an amine catalyst which does not have steric hindrance, thereby preparing cyclic polyester oligomers. However, prior art methods using an amine catalyst and corrosive acid chlorides such as terephthaloyl chloride are not preferable because those methods require chlorides that are disadvantageous in terms of the environment. In addition, an expensive recirculation process is required in relation to the formation of amine salt which is a byproduct.

[0007]

Furthermore, macrocyclic polyester oligomers proposed in Japanese Laid Open Patent Publication No. H8-225633 exhibit a low degree of viscosity and can be easily impregnated in a fine fibrous preform. Hence, they are receiving attentions as a matrix for composite materials. In addition, macrocyclic polyester oligomers are molten and polymerized at a much lower temperature than polymers to be obtained. Therefore, a molten flow, polymerization and crystallization can take place isothermally. Accordingly, it is pointed out that less time, costs and tools are required for thermal recycling. Polymers with a high degree of polymerization can be obtained by using cyclic

polyester oligomers, however, as for a reaction solvent needed for synthesizing cyclic polyester oligomers, it discloses only the point that having a higher temperature than the boiling point of diol which is generated as a byproduct in the reaction process of cyclic polyester oligomers is suitable for improving the yield. Therefore, to conduct a more economical production of polyester, just employing an expensive reaction solvent is not enough to enhance the economical efficiency and the productivity of prior art methods using a solid phase polymerization.

[0008]

Further, the production method of macrocyclic polyester oligomers proposed in Japanese Laid Open Patent Application Publication No. H9-296036 is to bring straight polyester into contact with an organic solvent which does not substantially contain oxygen or water and a depolymerization catalyst, thereby depolymerizing the straight polyester and generating macrocyclic polyester oligomers. An amine catalyst and conventionally known corrosive acid chlorides such as and terephthaloyl chloride are not used in this method and hence, it is advantageous in the environmental aspect. However, in the method to obtain cyclic polyester oligomers through depolymerizing straight polyester, simply using an expensive reaction solvent is not sufficient to improve the economical efficiency and the productivity, as mentioned in the above.

[0009]

Based on the background described in the above, it is desired to economically obtain polyester with a high degree of polymerization.

[0010]

[Issues that the Invention Attempts to Solve]

The purpose of the present invention is to eliminate the disadvantages in a synthesis of cyclic polyester oligomers mentioned in the above, and to provide an economical production method of cyclic polyester oligomers.

[0011]

[Means to Solve Issues]

The aforementioned purpose of the present invention is accomplished by a production method of cyclic polyester oligomers characterized in that in producing cyclic polyester oligomers from straight polyester oligomers that are obtained through an esterification reaction of dicarboxylic acid components and diol components, or from straight polyester, when at least a portion of a reaction solvent which is discharged from a reaction tank in which cyclic polyester oligomers are produced is put back to said reaction tank for repeated use, the amount of unreacted materials contained in the reaction solvent is 10% or less by weight.

[0012]

[Embodiments of the Invention]

Polyester of the present invention is not particularly limited as long as it is a polymer that is synthesized from a dicarboxylic acid or its ester formation derivative, and diol or its ester formation derivative, and as long as it can be used as shaped products such as fibers, films, bottles and the like.

[0013]

As concrete examples of such polyester, polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexylene dimethylene terephthalate, polyethylene-2, 6-naphthalene dicarboxylate, polyethylene-1, 2-bis (2-chlorophenoxy) ethane-4, 4'-dicarboxylate and the like can be cited. The present invention is especially suitable with polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate that are generally used, or with polyester copolymers which mainly contains polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate.

[0014]

As concrete examples of dicarboxylic acids that are used for obtaining such polyester, aromatic dicarboxylic acids including terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid and 4, 4'-diphenyl dicarboxylic acid, aliphatic dicarboxylic acids such as adipic acid and sebacic acid, and alicyclic dicarboxylic acids including cyclohexane dicarboxylic acid can be listed. Besides, examples of diol include ethylene glycol, propanediol, butanediol, neopentyl glycol, hexamethylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol and cyclohexane dimethanol.



[0015]

Furthermore, to such polyester, as copolymerization components, dicarboxylic acids and their ester formation derivatives such as adipic acid, isophthalic acid, sebacic acid, phthalic acid, and 4, 4'-diphenyl dicarboxylic acid, dioxy compounds such as polyethylene glycol, diethylene glycol, hexamethylene glycol, neopentyl glycol and polypropylene glycol, oxycarbonic acids and their ester formation derivatives including p-( $\beta$ -oxyethoxy) benzoic acid and lactic acid may be copolymerized.

[0016]

In the cyclic polyester oligomer production method of the present invention, cyclic polyester oligomers are produced using straight polyester oligomers obtained through an esterification reaction of dicarboxylic acid and diol (Method A), or using straight polyester (Method B). Besides, in the straight polyester, the intrinsic viscosity of polymer  $[\eta]$  is 0.4 or more, and those in which the intrinsic viscosity of polymer is less than 0.4 are considered to be straight polyester oligomers.

[0017]

First, in Method A, it is preferred from an economical standpoint to use a straight polyester oligomer for which when an esterification reaction of dicarboxylic acid and diol is conducted, the starting mole ratio of diol components and dicarboxylic acid components falls into a range of 1.0 ~ 1.6. At this point, when the starting mole ratio of diol components and dicarboxylic acid components is 1.0 or higher, the productivity is enhanced due to a reduced time period for the esterification reaction, and thus it is economically desirable. On the other hand, when the starting mole ratio is 1.6 or less, an average polymerization degree of straight polyester oligomers obtained through an esterification reaction becomes 2 or higher. As a result, to obtain cyclic polyester oligomers, till the time a preferable average polymerization degree is achieved, a process to remove excessive diol components is not required, and thus it is economically desirable. Therefore, more preferably, the starting mole

ratio of diol components/ dicarboxylic acid components to be in the range of 1.1 ~ 1.5, and even more preferably, in the range of 1.25 ~ 1.40.

[0018]

In the purpose of the present invention, for producing cyclic polyester oligomers economically, an esterification reaction of dicarboxylic acid and diol is conducted with the starting mole ratio of diol components/ dicarboxylic acid components in the range of 1.0 ~ 1.6. It is preferable to use straight polyester oligomers at the time when the esterification reaction in a continuous polymerization process is completed. Here, the continuous polymerization process includes three or more tanks including a conventionally known esterification reaction tank, a preliminary polymerization tank and a final polymerization tank. In the present invention, to use straight polyester oligomers at the time when the esterification reaction in the continuous polymerization process is completed, straight polyester oligomers that are processed through an esterification reaction tank in which the esterification process is substantially completed may be used, or those which passed through the subsequent preliminary polymerization tank can be employed. At this point, for a method of polycondensation in the preliminary polymerization tank, any one of the prior art methods can be applied. For instance, a method in which while raising the temperature of a reaction product under a reduced pressure, leaving diol components and other byproducts and the like are removed, and at the same time, a polymerization degree is increased up to a predetermined value can be applied. Or a method in which instead of reducing a pressure in a reaction system, an inert gas is supplied to increase a polymerization degree is increased and so forth can be applied.

[0019]

Further, it is preferable that the average polymerization degree of straight polyester oligomers at the time when the esterification reaction of dicarboxylic acid and diol conducted with the starting mole ratio of diol components/ dicarboxylic acid components in the range of 1.0 ~ 1.6 is completed, is 2 ~ 3. More desirably, the average polymerization degree is 2 ~ 10 and even more preferably it is 2.5 ~ 4.0. Hence, in order to obtain a desirable straight polyester oligomers, it is preferred to use those which passed through an esterification reaction tank in an continuous polymerization process. Regarding such a continuous polymerization process, a method may be employed in which in a continuous polymerization apparatus in that a prior art melt polycondensation process is conducted, a

branch pipe is provided for a reaction product solution transfer pipe between the esterification reaction tank and a preliminary polymerization tank, and the amount of solution transfer is controlled with a gear pump and so forth. Besides, in the continuous polymerization process for the process of producing cyclic polyester oligomers, an esterification reaction may be conducted.

[0020]

In the present invention, at any point before starting a synthesis of cyclic polyester oligomers, a conventionally known variety of esterification catalysts are added to a reaction system, and thereby a reaction speed of an esterification reaction is improved further. As a result, the reaction can be conducted more economically. However, it is not particularly limited because even if the esterification reaction is conducted without adding any esterification catalyst, the method of the present invention is economically superior compared to prior art methods of cyclic polyester oligomer production. As a specific example of an esterification catalyst compound, tin compound and/ or titanium compound is desirable. Furthermore, any point before the start of cyclic polyester oligomer synthesis indicates any point at the time of preparation of slurry of dicarboxylic acid and diol, and in the esterification reaction process.

[0021]

Examples of tin compound include, dibutyl tin oxide, stannous chloride, tin octylate, tin laurilate and monobutyl hydroxy tin oxide and so forth. These tin compounds can include those in which a plurality of tin compound molecules are associated or those which became oligomers with some changes.

[0022]

Moreover, as titanium compound, tetrabutyl titanate, tetraisopropyl titanate, tetrastearyl titanate, potassium titanyl oxalate, lithium titanyl oxalate and the like can be listed. Among them, a complex oxide whose main metallic element is a titanium compound, and a compound containing chelating agents whose main metallic element is a titanium compound are particularly preferred. Here, a complex oxide whose main metallic element is a titanium compound is, for example, produced from a titanium alkoxide compound and alkoxide compounds such as silicon, aluminum, zirconium, and germanium through the sol-gel process of coordination chemistry, however, it is not particularly limited. Furthermore, a compound containing chelating agents whose main metallic element is a titanium compound is, for instance, a titanium compound containing chelating agents such as

ethylenediamine tetraacetic acid, hydroxy ethyl iminodiacetic acid, diethylenetriamine pentaacetic acid, triethylene tetramine hexaacetic acid, citric acid, maleic acid or a mixture of these, however, it is not particularly limited.

[0023]

In addition, considering a reaction speed of an esterification reaction and a hue of polymers to be obtained in the end, the amount of esterification catalysts to be added is preferably 0.0001% by weight ~ 0.2% by weight in metal weight against polymers to be obtained. Further, it is even more desirable to be 0.0005% by weight ~ 0.1% by weight.

[0024]

On the other hand, in Method B, straight polyester may be produced with a prior art method, or recovered polyester may be used.

[0025]

In the present invention, when straight polyester oligomers or straight polyester mentioned in the above are used, as for a production method of cyclic polyester oligomers, a prior art method can be applied. However, it is necessary to repeatedly use at least a portion of a reaction solvent which is discharged from a reaction tank in which cyclic polyester oligomers are produced by putting it back to said reaction tank. At this point, it is required that the amount of unreacted materials contained in the reaction solvent is 10% by weight or less, considering a yield of cyclic polyester oligomers and an economical efficiency. More preferably, it is 5% by weight or less and even more desirably, it is 3% by weight. Moreover, unreacted materials contained in the reaction solvent indicate dicarboxylic acid components and diol components that are source materials, their byproducts and straight polyester oligomers.

[0026]

Here, regarding a reaction solvent and a cyclization catalyst, for instance in the synthesizing

method of cyclic polyester oligomers described in Polymer Letters (F. Lynn Hamb, 5 (1057), 1967), it is reported that as a reaction solvent 1-methylnaphthalene is used, and as a cyclization catalyst tetraisopropyl titanate is used. Furthermore, Japanese Laid Open Patent Application Publication H8-225633 suggests to employ a hydrocarbon compound such as ortho-terphenyl, meta-terphenyl or para-terphenyl and the like as a reaction solvent, and an organic tin compound and or a tetraalkoxy titanate including tetrabutyl titanate as a cyclization catalyst.

[0027]

Accordingly, as a reaction solvent used in the present invention, the one having a higher boiling point than that of diol which is generated as a byproduct in a reaction process of cyclic polyester oligomers, is suitable to improve an yield. Therefore, it is preferred that the reaction solvent is a compound with a carbon number of 6 or more. A reaction solvent with a carbon number of 10 or more is more desirable. To be specific, hydrocarbon compounds and mixtures of those such as 1-methylnaphthalene, 2-methylnaphthalene, 1, 4-dimethynaphthalene, 1, 7-dimethynaphthalene, 2, 6-dimethynaphthalene, 2, 7-dimethynaphthalene, ortho-terphenyl, meta-terphenyl, para-terphenyl and hexadecane can be used.

[0028]

In addition, for a cyclization catalyst, an organic tin compound and/ or tetraalkoxy titanate and so forth can be employed, but it is not particularly limited. Besides, in view of a reaction speed of cyclization reaction and an economical efficiency, the amount of cyclization catalysts to be added is preferably 0.01% by weight ~ 2% by weight in metal weight against cyclic polyester oligomers to be generated. Further, it is more desirable to be 0.1% by weight ~ 1% by weight.

[0029]

Furthermore, regarding the production method of cyclic polyester oligomers, a reaction product produced through method A or Method B is sent to a reaction tank for synthesizing cyclic polyester oligomers, and the reaction solvent and cyclization catalyst mentioned in the above can be used. A synthesis is conducted through a batch type polymerization process or a continuous polymerization process. An average residence time in said reaction tank is preferably 0.5 ~ 2 hours. Obtained reaction product is sent to a solvent removal tank, and the reaction solvent is removed. Consequently, it is sent

to a solid body precipitation tank, and by adding a hydrocarbon compound such as hexane, the reaction product contained in the solvent can be precipitated. Further, having obtained mixture pass through a centrifugal separator and a fluidized bed type dryer, and thereby separate it from a hydrocarbon compound including hexane, cyclic polyester oligomers can be obtained. At this point, removed reaction solvent is put back to said reaction tank and used repeatedly when the amount of unreacted materials contained in said reaction solvent is 10% by weight or less. Or, the amount of unreacted materials contained in said reaction solvent is made 10% by weight or less by passing through a fractionating column, then unreacted materials are put back to said reaction tank and used repeatedly. However, in said reaction tank, other than the recovered solvent mentioned in the above, a new reaction solvent can be employed.

[0030]

In the present invention, cyclic polyester oligomers that are produced using Method A or Method B are substantially pure. However, in many cases the purity is 60% or more, it is preferably 70% or more, and the purity of 80% or more is even more desirable. In addition, obtained cyclic polyester oligomers contain straight polyester oligomers at 10% or less, preferably at 5% or less, and the rate of 2% or less is even more preferred. Also, an average polymerization degree of obtained cyclic polyester oligomers is desired to be 2 ~ 10, and more preferably be 2 ~ 5.

[0031]

Besides, there are no restrictions for straight polyester oligomers or straight polyester to contain cyclic polyester oligomers.

[0032]

In the present invention, regarding the production of polyester using cyclic polyester oligomers and through open ring polymerization, as long as cyclic polyester oligomers are brought into contact with a catalyst for cyclic polyester oligomers, it can be conducted by a prior art method and not particularly limited.

[0033]

For instance, various types of organic tin compounds and titanate ester described in U.S. Patent Publications Nos. 5039783, 5214158 and 5231161 can be employed as catalysts for cyclic polyester oligomers, or cyclic titanium catalysts including di-(1-butyl)-2, 2-dimethylpropane-1, 3-dioxy titanate,

bis (2, 2-dimethyl-1, 3-propylene) titanate or 1-(1-butoxy)-4-methyl-2, 6, 7-trioxa-1-titanabicyclo [2, 2, 2] octane may be used as catalysts for cyclic polyester oligomers. In addition, antimony compounds and bismuth compounds mentioned in Macromolecules (Ji H. Youk, 33 (3594), 2000) can be employed as catalysts for cyclic polyester oligomers, but they are not particularly limited.

[0034]

Furthermore, in view of a reaction speed of open ring polymerization and a polymerization degree of generated polymers, the amount of catalysts for cyclic polyester oligomers to be added is preferably 0.0001% by weight ~ 1% by weight in metal weight against cyclic polyester oligomers used. Further, it is more desirable to be 0.001% by weight ~ 0.3% by weight. In the case in which the amount of catalysts to be added is 0.0001% by weight or less, since these catalysts are sensitive to impurities contained in cyclic polyester oligomers, especially water, hydroxy compounds and acidic impurities which contains carboxylic acid and its anhydride, when such impurities exist, some of the catalysts are deactivated. As a result, open ring polymerization may become imperfect, or polymers with a low degree of polymerization may be obtained. Moreover, when the amount of catalysts to be added is 1% by weight or more, a catalyst becomes a part of the end group of polymer. Therefore,

a growth reaction in open ring polymerization of cyclic polyester oligomers is inhibited and thus polymer with a low degree of polymerization may be obtained.

[0035]

In the present invention, as for the contact between cyclic polyester oligomers and a catalyst for cyclic polyester oligomers, a contact can be made in the range of 160 ~ 320 degrees Celsius. In order to enhance the solubility of cyclic polyester oligomers, polymerization may be conducted through mixing them with thermoplastic polymer in a molten state. Examples of thermoplastic polymers include addition polymers such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyvinylidene chloride, fluororesin, polymethyl methacrylate, condensation polymers including polyamide, polyester, polycarbonate, polyphenylene oxide, polyaddition polymers such as polyurethane, and open ring polymers such as polyacetal. Among them, polyester is desirable. In polyester, polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate that are widely used, and polyester copolymers which mainly contain polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate are particularly preferred.

[0036]

Further, when mixing cyclic polyester oligomers and thermoplastic polymers that are in a molten state, for polymers that passed through a preliminary polymerization tank or a final polymerization tank in a continuous polymerization process, such a method can be applied in that a static mixing device is provided in a reaction product pipe between said reaction tank and an open ring polymerization reaction tank, and cyclic polyester oligomers can be supplied through a branch pipe right before said device. Besides, thermoplastic polymers that passed through the final polymerization tank in the continuous polymerization process and then made into chips or existing thermoplastic polymers that are made into chips may be melted and mixed with cyclic polyester oligomers in an extruding machine. At this point, the extruding machine is not particularly limited, however, as examples of prior art machine, 1-axis type kneading machine, 2-axis type kneading machine and kneading machine with a vent and the like can be listed.

[0037]



In the present invention, in the case in that cyclic polyester oligomers and thermoplastic polymers that are in a molten state are mixed, it is desirable that the degree of intrinsic viscosity of obtained polyester is 0.65 or more, and polyester with a high polymerization degree of 0.70 or more is more preferable.

[0038]

Moreover, in the present invention, to improve thermal resistance and hue, prior art phosphorus compounds or cobalt compounds may be added to ultimately obtained polyester at any point. Further, in the present invention, if necessary, publicly known compounds, for example inorganic particles for frosting, antioxidant, heat insulator, antistatic agent, ultraviolet absorption agent and so forth can be added and contained.

[0039]

As described in the above, in the present invention, when repeatedly use at least a portion of a reaction solvent which is discharged from a reaction tank in which cyclic polyester oligomers are produced by putting it back to said reaction tank, the amount of unreacted materials contained in the reaction solvent is made 10% by weight or less. Therefore, it becomes possible to obtain polyester with a high degree of polymerization more economically compared to prior art solid phase polymerization processes or open ring polymerization processes.

[0040]

[Embodiments]

Using examples in the below, the present invention is explained further in detail. Besides, physical properties in examples were measured in methods explained below.

(1) Degree of intrinsic viscosity of polymers  $[\eta]$

Orthochlorophenol was used as a solvent and measurements were conducted at 25 degrees Celsius.

(2) Quantity of unreacted materials in reaction solvents

Calculations were conducted with liquid chromatography using ratio of peak surface areas for low polymers of each polymerization degree that is identified in advance (UV absorption standard : %).

(3) Purity and average polymerization degree of cyclic polyester oligomers

Calculations were conducted with liquid chromatography using ratio of peak surface areas for low polymers of each polymerization degree that is identified in advance (UV absorption standard : %).

[0041] Example 1

In a continuous polymerization device mainly containing a first esterification reaction tank, a second esterification reaction tank and a polycondensation reaction tank, slurry in which 16.6 part by weight of terephthalic acid and 8.2 part by weight of ethylene glycol were stirred and prepared beforehand was supplied into the first esterification reaction tank at the supplying speed of 23.8 part by weight/ hour. An average residence time at the first esterification reaction tank was 3 hours and 50 minutes, the reaction temperature was 250 degrees Celsius, the reaction pressure was  $1.013 \times 10^5$  Pa, and an average polymerization degree of obtained reaction products was 3.0. This process for producing straight polyester oligomers is called Process 1.

[0042]

These reaction products were continuously extracted, and sent to a reaction tank for synthesizing cyclic polyester oligomers. In this reaction tank, recovered  $\alpha$ -methylnaphthalene in which unreacted materials were contained at 2.5% by weight was used as a reaction solvent, and tetraisopropyl titanate was used as a catalyst. An average residence time in said reaction tank was 50 minutes. Obtained reaction products were sent to a solvent removing tank and  $\alpha$ -methylnaphthalene was removed. Subsequently, the reaction products were sent to a solid body precipitation tank, hexane was added, and thereby reaction products contained in the solvent precipitated. Obtained mixture was put through a centrifugal separator and a fluidized bed type dryer to be removed from hexane, and then cyclic polyester oligomers were obtained. This process to produce cyclic polyester oligomers is called Process 2. Moreover,  $\alpha$ -methylnaphthalene used as a reaction solvent was recovered and put back to the reaction tank.

[0043]

In addition, these reaction products were continuously extracted, and separately produced polyethylene terephthalate chips were supplied to a 2-axis type extruding machine so that the mixing ratio became oligomer/ polymer = 80/ 20. Further, as a catalyst for an open ring polymerization, tetraisopropyl titanate was added to the 2-axis type extruding machine. An average residence time at the 2-axis type extruding machine was 10 minutes, and the degree of intrinsic viscosity of obtained

polyethylene terephthalate was 1.31. This process to produce polyester through open ring polymerization is called Process 3.

[0044]

An average residence time required for Process 2 and thereafter was 1 hour, and it was possible to economically produce polyester with a high degree of polymerization.

[0045]      Example 2

In stead of the straight polyester oligomer synthesis in Process 1 of Examples 1, a synthesis of cyclic polyester oligomers was conducted using polyethylene terephthalate as a source material.

As a reaction solvent in Process 2, m-terphenyl in which unreacted materials were contained at 3.9% by weight was used. Polymers were polymerized in the same manner as in Example 1 except that oligomer/ polymer mixing ratio and types of polymers and catalysts used in Process 3 were changed.

[0046]

The degree of intrinsic viscosity of obtained polymers was 1.01 and an average residence time required for Process 2 and thereafter was 1 hour and 50 minutes. Polymer production was conducted within a time period that is economically superior.

[0047]      Example 3

Polymers were polymerized in the same manner as in Example 1 except that polybutylene terephthalate was used as a starting source material, and a reaction solvent, catalysts and so forth were changed.

[0048]

The degree of intrinsic viscosity of obtained polymers was 1.12 and an average residence time required for Process 2 and thereafter was 2 hours. Polymer production was conducted within a time period that is economically superior.

[0049]      Example 4

Polymers were polymerized in the same manner as in Example 1 except that propylene glycol and terephthalic acid were used as starting source materials, and a reaction solvent, catalysts and so forth were changed.

[0050]

The degree of intrinsic viscosity of obtained polymers was 1.05 and an average residence time required for Process 2 and thereafter was 1 hour and 1 minutes. Polymer production was conducted within a time period that is economically superior.

[0051] Comparative Example

A synthesis of cyclic oligomers was conducted using a reaction solvent which contains unreacted materials other than that of the present invention. As a result, the polymerization degree of polymers obtained in the end was low.

[0052]

[Table 1]

			Example 1	Example 2	Example 3	Example 4	Comparative Example
Process 1 (Straight oligomer synthesis or polyester type)	Reaction conditions	Source material (diol/ dicarboxylic acid or polyester)	Ethylene glycol/ terephthalic acid	Polyethylene terephthalate	Polyethylene terephthalate	Propylene glycol/ terephthalic acid	Ethylene glycol/ terephthalic acid
		Starting mole ratio	1.33	-	-	1.35	1.80
		Catalyst *1 (% by weight)	N/A	-	-	TBT 0.030	N/A
		Average residence time (hour : minute)	3:50	-	-	4:30	4:10
		Process type	Continuous polymerization	-	-	Batch polymerization	Batch polymerization
Process 2 (Cyclic oligomer synthesis)	Reaction conditions	Solvent	$\alpha$ -methylnaphthalane	m-terphenyl	$\alpha$ -methylnaphthalane	m-terphenyl	m-terphenyl
		Catalyst	TPT	TPT	MBO	TPT	MBO
	Average residence time (hour : minute)	0:50	1:30	1:50	1:00	2:30	
	Unreacted materials contained in reaction solvent (% by weight)		2.5	3.9	6.5	5.5	21
	Purity of cyclic oligomers (% by weight)		98	95	96	90	40
Process 3 (Open ring polymerization or polycondensation)	Reaction conditions	Average polymerization degree of cyclic oligomers	3.0	4.5	5.9	2.6	2.3
		Oligomer/ polymer ratio (Polymer type)	80/ 20 PET	70/ 30 PBT	50/ 50 PET	30/ 70 PPT	60/ 40 PET
		Catalyst *1	TPT	MBO	TPT	TPT	MBO
	Average residence time (hour : minute)	0:10	0:20	0:10	0:10	0:30	
	Intrinsic viscosity of polymer		1.31	1.01	1.12	1.05	0.54
Total of residence time in Process 2 and thereafter (hour : minute)			1:00	1:50	2:00	1:10	3:00

\*1 Catalyst: TBT = tetrabutyl titanate, MBO = monobutylhydroxy tin oxide, TPT = tetraisopropyl titanate

[0053]

[Advantages of the Invention]

The cyclic polyester oligomer production method of the present convention enables to obtain polyester with a high degree of polymerization more efficiently compared to prior art production methods.

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F term (reference) 4J029 AA03 AB04 AC01 AC02 AC04  
BA02 BA03 BA04 BA05 BA08  
BA09 BA10 BD07 BF09 BF25  
CA02 BA06 CB05 CB06 CB10  
CC05 CD00 JB023 JB043  
JF251 JF371 KE03 KE07  
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